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Spin Properties of Pair-Correlated Atomic and Molecular Singlet Wavefunctions

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The recent work of Sinanoğlu upon pair-correlated wavefunctions is considered. We derive the conditions required for his wavefunction to be a spin singlet, and then relate these conditions to his theory. In particular, we show them to be satisfied to an approximation consistent with those used in deriving his "exact pair" theory. An error in the original integral breakdown is also pointed out and shown to have little effect on the results of the theory.

Author

1. INTRODUCTION

The recent work of Sinanoğlu has revived interest in the possibility of treating electronic correlation in atomic and molecular systems by the specific introduction of pair correlation functions into the total wavefunction of the system. The value of such an approach for the case of two-electron systems has been known since the pioneering work of Hylleraas,[2] and it surely has occurred to many investigators that its application to larger systems might be useful.[3] The difficulty heretofore has been the apparent intractability of the resulting mathematics: once one introduces pair correlation functions into a wavefunction, the energy associated with the wavefunction contains several integral terms each involving more than one pair function. Assuming as a starting point a restricted Hartree–Fock calculation for closed shell systems and making particular use of a corollary of Brillouin's theorem,[4] due to Moller and Plesset,[5] Sinanoğlu has indicated that such terms can be expected to make small contributions to the energy. If the approximation is then made of ignoring these terms, the variation problem of determining the set of pair-correlation functions then separates into a set of independent variation problems, one for each pair-correlation function. Sinanoğlu has suggested that the latter simpler problems be used to determine the pair functions. However, the following question now arises: The symmetry properties of a wavefunction are properties of the wavefunction overall, and not just of parts of the wavefunction. If various parts are determined independently of one another, will the over-all wavefunction then exhibit the appropriate symmetries? In this paper we examine this question for a particularly important case; viz., we ask what conditions must be satisfied by the pair-correlation functions in order that the overall wavefunction be a spin singlet, and to what extent the prescription given by Sinanoğlu gives rise to pair correlation functions satisfying these conditions. The application of our method of approach to states of higher multiplicity is straightforward enough, but we do not consider it, since it would only complicate the discussion without adding any new insights. Similarly, we do not discuss other symmetry properties, e.g., angular momentum in atoms. We only remark that for any given system, questions similar to those we have phrased above must be asked for each symmetry property that the system possesses.

In the following sections, we explicitly discuss the singlet state of a *four* electron system, e.g., the Be atom or the LiH molecule. In point of fact, the results we derive are much more general, being applicable to *any* closed-shell singlet state generated by adding pair correlation terms to a restricted Hartree-Fock function. Inasmuch as larger systems require cumbersome notation, we omit general proofs (although we quote the results of such proofs below), and concentrate on the above-mentioned four-electron systems. The structure of the more general proof should become apparent to the reader from what follows.

In Sec. 2, we restate, for reference, Sinanoğlu's[1] basic ideas. In Sec. 3, we derive the spin conditions which his wavefunction must satisfy. In Sec. 4, we relate these conditions to his theory, and show, to the extent possible in an abstract analysis, the degree to

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[1] O. Sinanoğlu, (a) J. Chem. Phys. **36**, 706, 3198 (1962); (b) Proc. Roy. Soc. (London) **A260**, 379 (1961); (c) Phys. Rev. **122**, 491, 493 (1961).
[2] E. A. Hylleraas, Z. Physik **54**, 347 (1929).
[3] C. C. J. Roothaan and A. W. Weiss, Rev. Mod. Phys. **32**, 194 (1960); C. C. J. Roothaan and W. Kolos, *ibid.*, **32**, 205 (1960); for further reference see K. Kumar, *Perturbation Theory and the Nuclear Many Body Problem* (North-Holland Publishing Company, Amsterdam, The Netherlands, 1962).
[4] L. Brillouin, Actualités Sci. Ind. **71**, (1933).
[5] C. Moller and G. Plesset, J. Appl. Phys. **46**, 618 (1934).

which these conditions are satisfied. The final word, we see, depends upon a numerical analysis which has not yet been performed. We regard the primary function of this paper as a stressing of the need for examination of symmetry properties in theories involving pair correlated wavefunctions.

Finally, an Appendix is included in which we correct an error in the analysis of integrals contained in Ref. 1(a). This correction leads to terms of small magnitude which do not appear to affect the general conclusions of that theory.

2. REVIEW OF THE PAIR THEORY[1]

We consider a wavefunction

$$\psi=\phi_0+\chi_s+\chi_{ss}, \tag{1}$$

where ϕ_0 is a four-electron restricted Hartree–Fock singlet wavefunction, i.e., a single determinant wavefunction

$$\phi_0=(4!)^{-\frac{1}{2}}\det\{1(1),2(2),3(3),4(4)\}. \tag{2}$$

The numbers 1, 2, 3, 4 refer to the four orthonormal Hartree–Fock spin orbitals. Thus, for the Be atom, 1, 2, 3, 4 mean the $1s\alpha$, $1s\beta$, $2s\alpha$, and $2s\beta$ spin orbitals, respectively, whereas for the LiH molecule 1, 2, 3, and 4 mean the $1s_{\mathrm{Li}}\alpha$, $1s_{\mathrm{Li}}\beta$, $1\sigma\alpha$, and $1\sigma\beta$ spin orbitals, respectively. We assume these orbitals to be known from a previous Hartree–Fock calculation (as, indeed they are for the specific examples cited here).[6,7] The first pair-correlation term χ_s in (1) is given by[8]

$$\begin{aligned}\chi_s=2^{-\frac{1}{2}}\mathfrak{A}\{&\hat{u}_{12}(1,2)3(3)4(4)+\hat{u}_{13}(1,3)2(2)4(4)\\&+\hat{u}_{14}(1,4)2(2)3(3)+\hat{u}_{23}(2,3)1(1)4(4)\\&+\hat{u}_{24}(2,4)1(1)3(3)+\hat{u}_{34}(3,4)1(1)2(2)\},\end{aligned} \tag{3}$$

where $\mathfrak{A}$ is the four-particle antisymmetrizer and $\hat{u}_{ij}(i,j)$ is the antisymmetric pair correlation function between orbitals i and j. In keeping with the suggestions of Ref. 1, these functions are chosen so as to be strongly orthogonal to the *occupied* Hartree–Fock orbitals, i.e., the $\hat{u}_{ij}$'s are chosen so as to satisfy the conditions

$$\int\hat{u}_{ij}(i,j)k(i)d(i)=\int\hat{u}_{ij}(i,j)k(j)d(j)=0, \tag{4}$$

where $k=1$, 2, 3, or 4, and $\int\cdots d(i)$ denotes space integration plus spin summation over the coordinates of Electron i. At this point, the pair correlation functions are unknown, and it is the general purpose of the theory to determine them. The second correlation term in (1) is given by

$$\begin{aligned}\chi_{ss}=\tfrac{1}{2}\mathfrak{A}\{&\hat{u}_{12}(1,2)\hat{u}_{3,4}(3,4)+\hat{u}_{13}(1,3)\hat{u}_{24}(2,4)\\&+\hat{u}_{14}(1,4)\hat{u}_{23}(2,3)\},\end{aligned} \tag{5}$$

and so does not contain any pair functions not already contained in χ_s. The energy of the wavefunction (1) is

$$E=\langle\psi\mid H\mid\psi\rangle/\langle\psi\mid\psi\rangle, \tag{6}$$

where

$$H=-\tfrac{1}{2}\sum_{i=1}^{4}\nabla_i^2-\sum_{\alpha}z_\alpha\sum_i r_{i\alpha}^{-1}+\sum\sum_{1\leq i<j\leq 4}r_{ij}^{-1} \tag{7}$$

is the Hamiltonian of the system (here and throughout this paper, we use atomic units: $\hbar=m=e=1$). The sum over α in (7) is over the nuclei, whose charges are z_α, and the other symbols have their usual meanings. The key step in Ref. 1 lies in replacing the exact expression (6) by the approximation

$$E\cong E_{\mathrm{HF}}+\sum\sum_{1\leq i<j\leq 4}\epsilon_{ij}', \tag{8}$$

where E_{HF} is the Hartree–Fock energy, i.e., is given by

$$E_{\mathrm{HF}}=\langle\phi_0\mid H\mid\phi_0\rangle/\langle\phi_0\mid\phi_0\rangle, \tag{9}$$

and is, therefore a *constant* in what follows. In (8), ϵ_{ij}' is the "exact pair energy" for the pair of orbitals i, j. This quantity is given by

$$\epsilon_{ij}'\equiv\frac{2\langle\mathfrak{B}(i,j)\mid m_{ij}\mid\hat{u}_{ij}(i,j)\rangle+\langle\hat{u}_{ij}(i,j)\mid e_i+e_j+m_{ij}\mid\hat{u}_{ij}(i,j)\rangle}{1+\langle\hat{u}_{ij}(i,j)\mid\hat{u}_{ij}(i,j)\rangle}, \tag{10}$$

where

$$\mathfrak{B}(i,j)\equiv2^{-\frac{1}{2}}\{i(i)j(j)-i(j)j(i)\} \tag{11}$$

is an antisymmetric two-particle function, and the operators e_i and m_{ij} are defined as follows:

$$e_i\equiv-\tfrac{1}{2}\nabla_i^2+\sum_\alpha z_\alpha r_{i\alpha}^{-1}+V_i-\epsilon_i; \tag{12}$$

$$m_{ij}=r_{ij}^{-1}-\bar{S}_i(j)-\bar{S}_j(i)+J_{ij}-K_{ij}, \tag{13}$$

where ϵ_i is the Hartree–Fock orbital energy of orbital i, and J_{ij} and K_{ij} are the Coulomb and exchange integrals for orbitals i and j, i.e.,

$$J_{ij}\equiv\langle i(i)j(j)\mid r_{ij}^{-1}\mid i(i)j(j)\rangle, \tag{14}$$

$$K_{ij}\equiv\langle i(i)j(j)\mid r_{ij}^{-1}\mid j(i)i(j)\rangle. \tag{15}$$

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[6] C. C. J. Roothaan, L. M. Sachs, and A. W. Weiss, Rev. Mod. Phys. **32**, 186 (1960); R. E. Watson, Phys. Rev. **119**, 170 (1960).

[7] S. L. Kahalas and R. K. Nesbet, J. Chem. Phys. **39**, 529 (1963); A. M. Karo, *ibid.* **30**, 1241 (1959); B. J. Ransil, Rev. Mod. Phys. **32**, 239 (1960).

[8] Here and throughout this paper the subscripts such as 12 should be interpreted as 1, 2,—i.e., as referring to Orbitals 1 and 2 (and similarly for 13, 14, etc.). The commas are omitted to simplify the typography.

Thus ϵ_i, J_{ij}, and K_{ij} are constants whose values are known from the Hartree–Fock calculation of ϕ_0. Next, in (13), the *integral operator* $\bar{S}_i(j)$ represents the Hartree–Fock potential upon electron j due to orbital i, and is defined by

$$\bar{S}_i(j)=\int i(i)r_{ij}^{-1}(1-P_{ij})i(i)d(i), \qquad (16)$$

where P_{ij} is the permutation operator which permutes space and spin coordinates i and j. It is understood to operate prior to the integration over the coordinates (i). Finally, the operator V_i in (12) is the total Hartree–Fock potential acting on electron i, and is usually defined by

$$V_i(i)\equiv\sum_{j=1}^{4}\bar{S}_j(i) \qquad (i=1,2,3,4). \quad (17)$$

In a well-known way, the presence of the factor $(1-P_{ij})$ leads to a cancellation of the direct and exchange parts of (16) whenever $\bar{S}_i(j)$ acts upon $i(j)$, i.e., the identity

$$\bar{S}_i(j)i(j)\equiv 0 \qquad (i=1,2,3,4), \qquad (18)$$

holds. This means that as far as the determination of the Hartree–Fock states is concerned, the definition (17) can equally well be written as

$$V_i(i)\equiv{\sum_{j=1}^{4}}'\bar{S}_j(i) \qquad (i=1,2,3,4), \quad (19)$$

where now the prime means that the term $j=i$ is omitted from the sum. In those cases where V_i operates upon functions other than the Hartree–Fock function, the two definitions (17) and (19) are different, and a choice must be made. The definition (13) of the "correlation potential" used in Ref. 1 is consistent with the use of (19) rather than (17). Alternatively, if one uses (17) to define the Hartree–Fock potential, it becomes necessary to define the correlation potential not by (17), but rather by

$$m_{ij}=r_{ij}^{-1}-\bar{S}_i(j)-\bar{S}_j(i)-\bar{S}_i(i)-\bar{S}_j(j)+J_{ij}-K_{ij}, \qquad (20)$$

for consistency. Either choice of definition, i.e., either (13) and (19) or (20) and (17) lead to the same final result. We only mention these two alternatives here so that the reader be cognizant of this point.

For further details of the basic theory, the reader may consult Ref. 1. The essential point of interest here is the expressions (8), (9), (10), in which one sees that the energy associated with the wavefunction (1) has been approximated by a sum of terms (10) *each of which is a functional of one and only one pair function* $\hat{u}_{ij}$. Thus, the determination of any pair function is independent of the determination of every other pair function, with all necessary definitions given in terms of known quantities by (11) through (16) and by (19).

Finally, we should note that Sinanoğlu[1a] has also suggested that when the correlation between a pair of orbitals is weak, i.e., when

$$\langle\hat{u}_{ij}(i,j)\mid\hat{u}_{ij}(i,j)\rangle\ll 1 \qquad (21)$$

that the expression (10) may be further approximated by

$$\epsilon_{ij}'\cong 2\langle B(i,j)\mid m_{ij}\mid\hat{u}_{ij}(i,j)\rangle + \langle\hat{u}_{ij}(i,j)\mid e_i+e_j\mid\hat{u}_{ij}(i,j)\rangle. \quad (22)$$

It should be remarked that the form (22) is one which can be obtained by making a perturbation expansion about the Hartree–Fock state. Using the perturbation–variation approach to determine the first-order wavefunction (which is now given by χ_s in our notation), one finds that it is necessary to minimize independent pair energies of exactly the form (22). Inasmuch as it is easy to show that perturbation theory wavefunctions of any order satisfy the same symmetries as the zeroth order wavefunction (which is here ϕ_0), one knows that the use of (22) automatically will generate the appropriate symmetries, provided only that the trial pair functions $\hat{u}_{ij}$ have sufficient flexibility. Because of this, it is not necessary to consider (22) further, and our discussion will center upon the "exact pair" form (10).

The question stated in the introduction now arises: if we use (10) to determine the $\hat{u}_{ij}$'s, i.e., by independent variation of each ϵ_{ij}' with respect to the corresponding $\hat{u}_{ij}$, how can we be sure that the symmetry requirements upon the total wavefunction (1), which depend simultaneously upon *all* of the $\hat{u}_{ij}$'s, be satisfied? To see what this question means with respect to spin, we first must see what restrictions, if any, are placed upon the pair correlation function $\hat{u}_{ij}$ by the requirements that ψ satisfy the conditions for a spin singlet[9]:

$$S^2\psi=0, \qquad (23)$$

$$S_z\psi=0. \qquad (24)$$

3. SPIN CONDITIONS

The condition of the strong orthogonality (4) has a simple and useful interpretation in the language of configuration interaction. Briefly stated, it is that each $\hat{u}_{ij}$ can be written in the form

$$\hat{u}_{ij}(i,j)=\sum_{k\geq 5}\sum_{l\geq 5}a_{ij}^{kl}k(i)l(j), \qquad (25)$$

where the a's are constants. The sum in (25) contains only so-called "double-excitation" terms, i.e., terms in which *both* orbitals k and l are excited (unoccupied)

[9] A similar method of spin analysis has been applied by A. Brickstock and J. A. Pople, Phil. Mag. **44**, 697 (1953).

Hartree–Fock orbitals. The condition (4) specifically rules out the appearance of "single-excitation" terms of the type where $k\leq 4$ and $l\geq 5$ or vice versa, and the over-all antisymmetry of the wavefunction rules out other single excitation terms. The "zero-excitation" terms $k=i$, $l=j$ and $k=j$, $l=i$ are ruled out by the trivial requirement that χ_s and χ_{ss} be orthogonal to ϕ_0, and at most renormalize the wavefunction (1). Thus, (25) is the most general form of the $\hat{u}_{ij}$'s needed to satisfy (4). Therefore, the three terms ϕ_0, χ_s, and χ_{ss} of (1) are, respectively, zero-excitation, double-excitation, and quadruple-excitation terms. This means that in ϕ_0 all four electrons occupy the lowest two space-orbitals, in χ_s two electrons are in the lowest two space-orbitals, and in χ_{ss} no electrons are in the lowest two space orbitals, so that the three terms ϕ_0, χ_s, and χ_{ss} are mutually orthogonal *in space alone.* As a consequence each separately must satisfy (23) and (24). We have of course already chosen ϕ_0 to satisfy these criteria, so it need not be considered further. Let us therefore examine the meaning of the requirements

$$S^2\chi_s=0, \tag{26}$$

$$S_z\chi_s=0 \tag{27}$$

which χ_s must by itself satisfy. (We then return to χ_{ss}.)

The condition (27) is trivial. The most general forms which satisfy it are given by

$$\begin{aligned}
\hat{u}_{12}(1,2)&=2^{-\frac{1}{2}}\mathcal{B}_{12}p_{12}(1,2)\alpha(1)\beta(2);\\
\hat{u}_{13}(1,3)&=2^{-\frac{1}{2}}\mathcal{B}_{13}p_{13}(1,3)\alpha(1)\alpha(3);\\
\hat{u}_{14}(1,4)&=2^{-\frac{1}{2}}\mathcal{B}_{14}p_{14}(1,4)\alpha(1)\beta(4);\\
\hat{u}_{23}(2,3)&=2^{-\frac{1}{2}}\mathcal{B}_{23}p_{23}(2,3)\beta(2)\alpha(3);\\
\hat{u}_{24}(2,4)&=2^{-\frac{1}{2}}\mathcal{B}_{24}p_{24}(2,4)\beta(2)\beta(4);\\
\hat{u}_{34}(3,4)&=2^{-\frac{1}{2}}\mathcal{B}_{34}p_{34}(3,4)\alpha(3)\beta(4),
\end{aligned} \tag{28}$$

where the p_{ij}'s are the parts of the $\hat{u}_{ij}$'s dependent upon the space coordinates. The operators $2^{-\frac{1}{2}}\mathcal{B}_{ij}$ in (28) select the antisymmetric components of the various expressions. The symmetric components are not needed, since they would in any case be removed by the operator $\mathcal{a}$ in expression (3). Using the relation $\mathcal{a}\mathcal{B}_{ij}=2^{\frac{1}{2}}\mathcal{a}$, we then have

$$\begin{aligned}
\chi_s=2^{-\frac{1}{2}}\mathcal{a}\alpha(1)\beta(2)\alpha(3)\beta(4)\{&p_{12}(1,2)\phi_2(3)\phi_2(4)\\
&+p_{13}(1,3)\phi_1(2)\phi_2(4)+p_{14}(1,4)\phi_1(2)\phi_2(3)\\
&+p_{23}(2,3)\phi_1(1)\phi_2(4)+p_{24}(2,4)\phi_1(1)\phi_2(3)\\
&+p_{34}(3,4)\phi_1(1)\phi_1(2)\},
\end{aligned}$$

where ϕ_1 and ϕ_2 are the two space orbitals, e.g., $\phi_1=1s$ and $\phi_2=2s$ for Be; and $\phi_1=1s_{\mathrm{Li}}$ and $\phi_2=1\sigma$ for LiH. Summing (4) over spin, the strong orthogonality becomes

$$\int_\Omega p_{ij}(i,j)\phi_k(i)d(i)=\int_\Omega p_{ij}(i,j)\phi_k(j)d(j)=0, \tag{30}$$

where $k=1$ or 2 and $\int\cdots d(i)$ means integration over space coordinates of (i). In terms of configuration interaction, this means that each p_{ij} may be written in the form

$$p_{ij}(i,j)=\sum_{k\geq 3}\sum_{l\geq 3}b_{ij}{}^{kl}\phi_k(i)\phi_l(j), \tag{31}$$

which is the space-only analog of (25), the b's of (31) being constants and the ϕ's the excited (unoccupied) Hartree–Fock space orbitals.

From (29) and (31), one sees that the term of (29) containing p_{12} is orthogonal in space alone to the remaining terms of χ_s. As a result this term separately must satisfy

$$S^2\{2^{-\frac{1}{2}}\mathcal{a}\alpha(1)\beta(2)\alpha(3)\beta(4)p_{12}(1,2)\phi_2(3)\phi_2(4)\}=0 \tag{32}$$

if χ_s is to satisfy (26). If we write $p_{12}(1,2)$ as a sum of a symmetric and an antisymmetric part

$$p_{12}(1,2)=p_{12}{}^S(1,2)+p_{12}{}^A(1,2), \tag{33}$$

where

$$\left.\begin{aligned}
p_{12}{}^S(1,2)&=p_{12}{}^S(2,1);\\
p_{12}{}^A(1,2)&=-p_{12}{}^A(2,1),
\end{aligned}\right\} \tag{34}$$

then it is well known and easy to prove that the $p_{12}{}^S$ part gives rise to a singlet whereas the $p_{12}{}^A$ part gives rise to a triplet. Thus, to satisfy (26), we must choose $p_{12}{}^A=0$. Similarly, we conclude $p_{34}{}^A=0$. More generally, for an N-electron system in a singlet state generated by excitations from a state with two electrons per space orbital, we must always have

$$p_{2i-1,2i}(1,2)=p_{2i-1,2i}(2,1), \tag{35}$$

i.e., the pair correlation function for the two electrons in the *same* space orbital is always a symmetric function with respect to coordinate interchange. This result, though important in applications, is not of particular interest here. It is when we turn to the remaining terms of χ_s, i.e., those involving p_{13}, p_{14}, p_{23}, and p_{24} that more interesting results appear. Because these terms are *not* orthogonal in space to each other, they must be treated as a group.

Assuming that p_{12} and p_{34} are chosen symmetric, then Condition (26) reduces identically to the criterion that the quantity

$$\begin{aligned}
W\equiv S^2\mathcal{a}\alpha(1)\beta(2)\alpha(3)\beta(4)\{&p_{13}(1,3)\phi_1(2)\phi_2(4)\\
&+p_{14}(1,4)\phi_1(2)\phi_2(3)+p_{23}(2,3)\phi_1(1)\phi_2(4)\\
&+p_{24}(2,4)\phi_1(1)\phi_2(3)\}
\end{aligned} \tag{36}$$

vanish identically. It is convenient to analyze the product in terms of the six four-electron bond eigenfunctions.[10]

$$\theta_{11}=\alpha\beta\alpha\beta-\beta\alpha\alpha\beta-\alpha\beta\beta\alpha+\beta\alpha\beta\alpha,$$

$$\theta_{12}=\alpha\alpha\beta\beta-\alpha\beta\alpha\beta-\beta\alpha\beta\alpha+\beta\beta\alpha\alpha,$$

$$\theta_{31}=\alpha\beta\alpha\beta-\beta\alpha\alpha\beta+\alpha\beta\beta\alpha-\beta\alpha\beta\alpha,$$

$$\theta_{32}=\alpha\alpha\beta\beta-\alpha\beta\alpha\beta+\beta\alpha\beta\alpha-\beta\beta\alpha\alpha,$$

$$\theta_{33}=\alpha\beta\alpha\beta+\beta\alpha\alpha\beta-\alpha\beta\beta\alpha-\beta\alpha\beta\alpha,$$

$$\theta_{51}=\alpha\alpha\beta\beta+\alpha\beta\alpha\beta+\beta\alpha\alpha\beta+\alpha\beta\beta\alpha+\beta\alpha\beta\alpha+\beta\beta\alpha\alpha, \quad (37)$$

where $\alpha\beta\alpha\beta$ means $\alpha(1)\beta(2)\alpha(3)\beta(4)$, etc. Of these θ_{11} and θ_{12} are singlets, θ_{31}, θ_{32}, θ_{33} are triplets, and θ_{51} is a quintet. One easily finds

$$\alpha\beta\alpha\beta=\tfrac{1}{6}(\theta_{11}-\theta_{12})+\tfrac{1}{4}(\theta_{31}+\theta_{33})+\tfrac{1}{6}\theta_{51}, \quad (38)$$

the triplet θ_{32} not appearing.

Since S^2 and $\mathfrak{A}$ commute, it is easy to reduce (36) to the form

$$\begin{aligned}W=\mathfrak{A}[\tfrac{1}{2}(\theta_{31}+\theta_{33})+\theta_{51}]\{&p_{13}{}^A(1,3)\phi_1(2)\phi_2(4)\\&+p_{24}{}^A(2,4)\phi_1(1)\phi_2(3)+p_{14}{}^S(1,4)\phi_1(2)\phi_2(3)\\&+p_{14}{}^A(1,4)\phi_1(2)\phi_2(3)+p_{23}{}^S(2,3)\phi_1(1)\phi_2(4)\\&+p_{23}{}^A(2,3)\phi_1(1)\phi_2(4)\},\end{aligned} \quad (39)$$

where we have again split the p_{ij}'s into symmetric and antisymmetric parts similar to (34). We note that the terms $p_{13}{}^S$ and $p_{24}{}^S$ do not appear, as they are projected out by the operators $\mathfrak{B}_{13}$ and $\mathfrak{B}_{24}$ in (28). In order to reduce (39) to a useful form, it is necessary that all p_{ij}'s contain the same coordinates, that all ϕ_1's contain the same coordinate, and that all ϕ_2's contain the same coordinate. Let us choose to write each term in the bracket in (39) in the form $p(1,3)\phi_1(2)\phi_2(4)$ so that the first term already is suitable. Consider now the second term. Using the operator identify

$$\mathfrak{A}\equiv P_{12}P_{34}\mathfrak{A}, \quad (40)$$

the commutability of the permutation operators P_{ij} with the antisymmetrizer $\mathfrak{A}$, and the fact that the effect of a permutation operator acting upon a function of space and spin is the direct product of the permutation of the space coordinates with that of the spin coordinates, the following identity is easily established:

$$\begin{aligned}&\mathfrak{A}[\tfrac{1}{2}(\theta_{31}+\theta_{33})+\theta_{51}]p_{24}{}^A(2,4)\phi_1(1)\phi_2(3)\\&\quad\equiv\mathfrak{A}[-\tfrac{1}{2}(\theta_{31}+\theta_{33})+\theta_{51}]p_{24}{}^A(1,3)\phi_1(2)\phi_2(4).\end{aligned} \quad (41)$$

Similar manipulations may be performed upon the remaining terms of (39), and lead to rewriting (39) in the form

$$\begin{aligned}W\equiv\mathfrak{A}Q=&-\tfrac{1}{2}\mathfrak{A}(\theta_{31}-\theta_{33})\\&\times[p_{14}{}^S(1,3)-p_{23}{}^S(1,3)-p_{14}{}^A(1,3)+p_{23}{}^A(1,3)]\\&\times\phi_1(2)\phi_2(4)+\tfrac{1}{2}\mathfrak{A}(\theta_{31}+\theta_{33})[p_{13}{}^A(1,3)-p_{24}{}^A(1,3)]\\&\times\phi_1(2)\phi_2(4)+\mathfrak{A}\theta_{51}\\&\times[p_{13}{}^A(1,3)-p_{14}{}^A(1,3)-p_{23}{}^A(1,3)+p_{24}{}^A(1,3)]\\&\times\phi_1(2)\phi_2(4),\end{aligned} \quad (42)$$

where Q is the spin-space function which stands to the right of $\mathfrak{A}$. Of all the 4! permutations of Q introduced by $\mathfrak{A}$, we need only consider the two given by $(1-P_{13})$. This is because all other permutations give rise to terms which are orthogonal in space alone to Q itself, so that W will vanish identically if and only if $(1-P_{13})Q$ vanishes identically. Using (37) and (42), we easily find

$$\begin{aligned}(1-P_{13})Q\equiv&-(\theta_{31}+\theta_{32})[p_{14}{}^S(1,3)-p_{23}{}^S(1,3)]\\&\times\phi_1(2)\phi_2(4)-(\theta_{32}+\theta_{33})[p_{14}{}^A(1,3)-p_{23}{}^A(1,3)]\\&\times\phi_1(2)\phi_2(4)+(\theta_{31}+\theta_{33})[p_{13}{}^A(1,3)-p_{24}{}^A(1,3)]\\&\times\phi_1(2)\phi_2(4)+2\theta_{51}[p_{13}{}^A(1,3)-p_{14}{}^A(1,3)\\&-p_{23}{}^A(1,3)+p_{24}{}^A(1,3)]\phi_1(2)\phi_2(4).\end{aligned} \quad (43)$$

Inasmuch as the four spin functions $\theta_{31}+\theta_{32}$, $\theta_{31}+\theta_{33}$, $\theta_{32}+\theta_{33}$ and θ_{51} in (43) are linearly independent, it follows that $(1-P_{13})Q$ (and hence W) can vanish identically if and only if the four space function coefficients in (43) separately vanish. Thus, since $\phi_1(2)\phi_2(4)\neq 0$ we see that (26) holds if and only if the following relations are satisfied:

$$p_{14}{}^S(1,3)=p_{23}{}^S(1,3), \quad (44)$$

$$p_{14}{}^A(1,3)=p_{23}{}^A(1,3), \quad (45)$$

$$p_{13}{}^A(1,3)=p_{24}{}^A(1,3), \quad (46)$$

$$p_{13}{}^A(1,3)-p_{14}{}^A(1,3)-p_{23}{}^A(1,3)+p_{24}{}^A(1,3)=0. \quad (47)$$

The three relations (44), (45), (46) are hardly surprising: they are simple consequences of the physical symmetry of the wavefunction and could have been guessed without any analysis. For example, (46) states that the space part of the $1s\alpha$–$2s\alpha$ correlation function (for Be) is the same as the space part of the $1s\beta$–$2s\beta$ correlation function. In terms of the vector model, it states that we can add two triplet correlation functions [Ref. 43] so as to form a singlet. The relation (47) is more interesting: it states that we can add four quintets to form a singlet, which is, again, not surprising. However, unlike (44), (45), (46), it does not appear that (47) might have been guessed without the analysis given here. We also note that (44) and (45) can be used to rewrite (47) as

$$p_{13}{}^A(1,3)=p_{14}{}^A(1,3), \quad (48)$$

[10] H. Eyring, J. Walter, and G. E. Kimball, *Quantum Chemistry* (John Wiley & Sons, Inc., New York, 1944), Chap. 13.

which is the primary result we have sought in this section. The implication of (44) to (47), and particularly (48), is that the four pair correlation functions between two different orbitals are not independent, but must be interrelated because of the spin character of the complete wavefunction. In the next section, we will see what this means in terms of the independent pair variation implied by (10).

Now we must examine the quadrupole excitation term χ_{ss} of (1). Here the situation is very simple. We substitute the relations (44) to (46) and (48), plus the requirements that p_{12} and p_{34} be symmetric into (28), and then substitute (28) into (5), so as to write χ_s in terms of the p_{ij}^S and p_{ij}^A. We then operate upon χ_{ss} with S^2. We find, by straightforward and simple algebra, which we omit for brevity, that $S^2\chi_{ss}=0$. That is to say, the conditions (44) to (46) and (48) not only guarantee that χ_s is a singlet, but they also guarantee that χ_{ss} is a singlet as well! Thus, these are the only conditions placed upon the pair functions by the requirement that ψ be a singlet, at least for the four electron problem.

If $N>4$, we note that relations like (44) to (48) may be derived for the pair correlation functions (we omit the proof, which is similar to that above). These relations are summarized in Table I. If the pair functions satisfy these relations we are guaranteed that the wavefunction $\psi=\phi_0+\chi_s+\chi_{ss}$ is a spin singlet.

4. RELATION OF SPIN CONDITIONS TO PAIR THEORY

Let us now investigate whether the Sinanoğlu "exact pair" energies (10) lead to (44) to (46) and (48) for a sufficiently flexible variation function. If the "exact" energies (10) are written in terms of the p_{ij}^S and p_{ij}^A and the spins are summed out, we immediately obtain (44) to (46) for the *intershell* functions. This follows from the fact that the pairs of equal functions of (44) to (46) satisfy the same equations. The symmetric nature of the *intrashell* spatial correlation functions is obvious. For example, consider the $\hat{u}_{12}$ correlation function. Although it can have both singlet and triplet spin components, only the singlet component can mix with ϕ_0 and thereby lower the energy. This implies that the p_{12}^A part must vanish to minimize the energy.

At this point, we are still left with the question as to whether or not independent variation of $\hat{u}_{13}$ and $\hat{u}_{14}$ meets the criterion (48). To answer this, we must specifically work out the 1, 3 and 1, 4 terms of Sinanoğlu's "exact pair" energies (10) making use of the decomposition (28) plus the decomposition of the p_{ij} into symmetric and antisymmetric parts. Thus we consider the terms

$$\epsilon_{13}'=\frac{2\langle\mathcal{B}(1,3)\mid m_{13}\mid\hat{u}_{13}\rangle+\langle\hat{u}_{13}\mid e_1+e_3+m_{13}\mid\hat{u}_{13}\rangle}{1+\langle\hat{u}_{13}\mid\hat{u}_{13}\rangle};\quad(49)$$

$$\epsilon_{14}'=\frac{2\langle\mathcal{B}(1,4)\mid m_{14}\mid\hat{u}_{14}\rangle+\langle\hat{u}_{14}\mid e_1+e_4+m_{14}\mid\hat{u}_{14}\rangle}{1+\langle\hat{u}_{14}\mid\hat{u}_{14}\rangle}.\quad(50)$$

The necessary and sufficient conditions that (48) be satisfied are:

(A) ϵ_{14}' must be a sum of two parts, the first a functional of p_{14}^S and not of p_{14}^A, and the second a functional of p_{14}^A and not of p_{14}^S.

(B) The part of ϵ_{14}' which is a functional of p_{14}^A must be the same functional of p_{14}^A as ϵ_{13}' is of p_{13}^A, except possibly for a constant multiplicative factor, whose value is immaterial. Substituting (28) into (49) and (50), we find, after some algebra, that

$$\epsilon_{13}'=N_{13}/\Delta_{13},\quad(51)$$

$$\epsilon_{14}'=N_{14}/\Delta_{14},\quad(52)$$

where

$$\begin{aligned}N_{13}=2\langle\mathcal{B}_{13}\phi_1(1)\phi_2(3)\mid r_{13}^{-1}\mid p_{13}^A(1,3)\rangle&\\+(J_{13}-K_{13})\langle p_{13}^A(1,3)\mid p_{13}^A(1,3)\rangle&\\+\langle p_{13}^A(1,3)\mid\tau(1)+\tau(3)-\epsilon_1-\epsilon_3+r_{13}^{-1}\mid p_{13}^A(1,3)\rangle&\\+\langle p_{13}^A(1,3)\phi_1(2)\mid r_{12}^{-1}+r_{23}^{-1}\mid p_{13}^A(1,3)\phi_1(2)\rangle&\\+\langle p_{13}^A(1,3)\phi_2(4)\mid r_{14}^{-1}+r_{34}^{-1}\mid p_{13}^A(1,3)\phi_2(4)\rangle,&\quad(53)\end{aligned}$$

$$N_{14}=N_{14}^A+N_{14}^S+N_{14}^{AS},\quad(54)$$

$$\begin{aligned}N_{14}^A=\langle\mathcal{B}_{14}\phi_1(1)\phi_2(4)\mid r_{14}^{-1}\mid p_{14}^A(1,4)\rangle+\tfrac{1}{2}\langle p_{14}^A(1,4)\mid\tau(1)+\tau(4)-\epsilon_1-\epsilon_4+J_{14}+r_{14}^{-1}\mid p_{14}^A(1,4)\rangle&\\+\tfrac{1}{2}\langle p_{14}^A(1,4)\phi_1(2)\mid r_{12}^{-1}+r_{24}^{-1}\mid p_{14}^A(1,4)\phi_1(2)\rangle+\tfrac{1}{2}\langle p_{14}^A(1,4)\phi_2(3)\mid r_{13}^{-1}+r_{34}^{-1}\mid p_{14}^A(1,4)\phi_2(3)\rangle&\\-\tfrac{1}{2}\langle p_{14}^A(1,4)\phi_1(2)\mid r_{24}^{-1}\mid p_{14}^A(1,2)\phi_1(4)\rangle-\tfrac{1}{2}\langle p_{14}^A(1,4)\phi_2(3)\mid r_{13}^{-1}\mid p_{14}^A(3,4)\phi_2(1)\rangle,&\quad(55)\end{aligned}$$

$$\begin{aligned}N_{14}^S=\langle C_{14}\phi_1(1)\phi_2(4)\mid r_{14}^{-1}\mid p_{14}^S(1,4)\rangle+\tfrac{1}{2}\langle p_{14}^S(1,4)\mid\tau(1)+\tau(4)-\epsilon_1-\epsilon_4+J_{14}+r_{14}^{-1}\mid p_{14}^S(1,4)\rangle&\\+\tfrac{1}{2}\langle p_{14}^S(1,4)\phi_1(2)\mid r_{12}^{-1}+r_{24}^{-1}\mid p_{14}^S(1,4)\phi_1(2)\rangle+\tfrac{1}{2}\langle p_{14}^S(1,4)\phi_2(3)\mid r_{13}^{-1}+r_{34}^{-1}\mid p_{14}^S(1,4)\phi_2(3)\rangle&\\-\tfrac{1}{2}\langle p_{14}^S(1,4)\phi_1(2)\mid r_{24}^{-1}\mid p_{14}^S(1,2)\phi_1(4)\rangle-\tfrac{1}{2}\langle p_{14}^S(1,4)\phi_2(3)\mid r_{13}^{-1}\mid p_{14}^S(3,4)\phi_2(1)\rangle,&\quad(56)\end{aligned}$$

$$N_{14}^{AS}=-\langle p_{14}^S(1,4)\phi_1(2)\mid r_{24}^{-1}\mid p_{14}^A(1,2)\phi_1(4)\rangle-\langle p_{14}^S(1,4)\phi_2(3)\mid r_{13}^{-1}\mid p_{14}^A(3,4)\phi_2(1)\rangle,\quad(57)$$

$$\Delta_{13}=1+\langle p_{13}^A(1,3)\mid p_{13}^A(1,3)\rangle,\quad(58)$$

$$\Delta_{14}=1+\tfrac{1}{2}\langle p_{14}^A(1,4)\mid p_{14}^A(1,4)\rangle+\tfrac{1}{2}\langle p_{14}^S(1,4)\mid p_{14}^S(1,4)\rangle.\quad(59)$$

In these expressions, all integrations are over space alone; $\mathcal{B}_{ij}=2^{-\frac{1}{2}}(1-P_{ij})$ and $C_{ij}=2^{-\frac{1}{2}}(1+P_{ij})$ are the two-particle antisymmetrizer and symmetrizer, respectively, acting in space alone, and the operator

$$\tau(i)=-\tfrac{1}{2}\nabla_i^2-\sum_\alpha z_\alpha r_{i\alpha}^{-1} \tag{60}$$

is the kinetic energy plus nuclear attraction for Electron i in atomic units. Utilizing the relations $\epsilon_3=\epsilon_4$ and $J_{13}=J_{14}$ we see that most of the terms of N_{13} are functionally equivalent to $N_{14}{}^A$; nevertheless, the two expressions are not functionally identical. In addition, the term $N_{14}{}^{AS}$ which occurs in N_{14} has no counterpart in N_{13}. Finally, the denominators Δ_{13} and Δ_{14} are not functionally identical. Consequently, independent variation of $\hat{u}_{13}$ and $\hat{u}_{14}$ cannot satisfy (24) exactly. On the other hand, it appears that the discrepancy is small. To see this, we introduce the *functionals*

$$\begin{aligned} f_1(p)=2\langle\mathcal{B}_{13}\phi_1(1)\phi_2(3)\mid r_{13}^{-1}\mid p(1,3)\rangle &+\langle p(1,3)\mid\tau(1)+\tau(3)-\epsilon_1-\epsilon_3+r_{13}^{-1}\mid p(1,3)\rangle \\ &+(J_{13}-K_{13})\langle p(1,3)\mid p(1,3)\rangle \\ &+\langle p(1,3)\phi_1(2)\mid r_{12}^{-1}+r_{23}^{-1}\mid p(1,3)\phi_1(2)\rangle \\ &+\langle p(1,3)\phi_2(2)\mid r_{12}^{-1}+r_{23}^{-1}\mid p(1,3)\phi_2(2)\rangle, \end{aligned} \tag{61}$$

$$\begin{aligned} f_2(p)=K_{13}\langle p(1,3)\mid p(1,3)\rangle &-\langle p(1,3)\phi_1(2)\mid r_{23}^{-1}\mid p(1,2)\phi_1(3)\rangle \\ &-\langle p(1,3)\phi_2(2)\mid r_{23}^{-1}\mid p(1,2)\phi_2(3)\rangle, \end{aligned} \tag{62}$$

$$g(p)=1+\langle p(1,3)\mid p(1,3)\rangle, \tag{63}$$

in terms of which

$$\epsilon_{13}'=f_1(p_{13}{}^A)/g(p_{13}{}^A), \tag{64}$$

and

$$\epsilon_{14}'=\frac{\frac{1}{2}f_1(p_{14}{}^A)+\frac{1}{2}f_2(p_{14}{}^A)}{g(p_{14}{}^A)+\frac{1}{2}\{\langle p_{14}{}^S(1,4)\mid p_{14}{}^S(1,4)\rangle-\langle p_{14}{}^A(1,4)\mid p_{14}{}^A(1,4)\rangle\}}+\frac{N_{14}{}^{AS}}{\Delta_{14}} + \frac{N_{14}{}^S}{g(p_{14}{}^S)-\frac{1}{2}\{\langle p_{14}{}^S(1,4)\mid p_{14}{}^S(1,4)\rangle-\langle p_{14}{}^A(1,4)\mid p_{14}{}^A(1,4)\rangle\}}. \tag{65}$$

In arriving at the expressions for ϵ_{13}' and ϵ_{14}', Sinanoğlu[1a] made two key approximations, viz., (1) The range of the correlation functions $\hat{u}_{ij}$ is short (the range of the $\hat{u}_{ij}$ naturally is the range of the space parts p_{ij} of the $\hat{u}_{ij}$'s). (2) The magnitude of the correlation terms χ_s and χ_{ss} are much less than that of ϕ_0, the Hartree–Fock term.

Using these approximations, we can simplify (65): First, using (1) one finds that the term $N_{14}{}^{AS}/\Delta_{14}$ in (65) is negligible compared to the other terms. Second, using (2) we can neglect the term

$$\tfrac{1}{2}\{\langle p_{14}{}^S(1,4)\mid p_{14}{}^S(1,4)\rangle-\langle p_{14}{}^A(1,4)\mid p_{14}{}^A(1,4)\rangle\}$$

in the remaining denominators, since it will be much less than $g\cong 1$. Thus (65) reduces to

$$\epsilon_{14}'\cong\frac{\frac{1}{2}f_1(p_{14}{}^A)+\frac{1}{2}f_2(p_{14}{}^A)}{g(p_{14}{}^A)}+\frac{N_{14}{}^S}{g(p_{14}{}^S)} \tag{66}$$

so that Condition (A) above is satisfied. We also see that Condition (B) is satisfied, with the multiplicative factor equal to $\frac{1}{2}$, provided f_2 is negligible in comparison with f_1. Examination of (61) and (62) shows that this is *probably* true: using Sinanoğlu's two assumptions all three terms of f_2 are small, i.e., they are of the type he neglected in obtaining the expression[1a] for ϵ_{ij}'. The terms of f_1, on the other hand, cannot *all* be neglected by use of the two approximations. In particular, we notice that f_1 includes among others *all* the terms arising from perturbation theory, [compare with (22)], which is known to yield the intershell correlation energy[11] to high accuracy. This indicates that it is very likely true that the conditions $S^2\psi=0$, $S_z\psi=0$ are satisfied to an order of approximation equivalent to that made in obtaining the energy expressions (8), (9), and (10).

It should be remarked that arguments of the above type cannot be expected to be absolutely conclusive either for arbitrary systems or even for our specific examples—the Be atom and the LiH molecule. The ultimate check is numerical calculation, where our anticipation is that these conclusions will prove valid for tightly bound systems.

Finally, we note that an alternate treatment of the spin is available. Thus, we can substitute the conditions (44) to (46) and (48), plus the symmetry of p_{12} and p_{34}, into the exact variational energy expression

TABLE I. Relations between pair functions for singlet states.

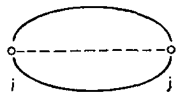
Pair function	Symmetric space part	Antisymmetric space part	Special relations
$\hat{u}_{2i-1,2i}$	$p^S{}_{2i-1,2i}\neq 0$	$p^A{}_{2i-1,2i}=0$	None
$\hat{u}_{2i-1,2j-1}$	$p^S{}_{2i-1,2j-1}=0$	$p^A{}_{2i-1,2j-1}\neq 0$	$p^A{}_{2i-1,2j-1}=p^A{}_{2i,2j}$
$\hat{u}_{2i-1,2j}$	$p^S{}_{2i-1,2j}\neq 0$	$p^A{}_{2i-1,2j}\neq 0$	$p^A{}_{2i-1,2j}=p^A{}_{2i,2j-1}$ $p^A{}_{2i-1,2j}=p^A{}_{2i-1,2j-1}$
$\hat{u}_{2i,2j-1}$	$p^S{}_{2i,2j-1}\neq 0$	$p^A{}_{2i,2j-1}\neq 0$	$p^S{}_{2i,2j-1}=p^S{}_{2i-1,2j}$
$\hat{u}_{2i,2j}$	$p^S{}_{2i,2j}=0$	$p^A{}_{2i,2j}\neq 0$ $(i\neq j)$	

[11] See, e.g., R. E. Watson, Phys. Rev. **119**, 170 (1960) for an analysis of the Be atom correlation energy and its relation to perturbation theory. This problem has also been considered by H. Kelly, Phys. Rev. (to be published).

for the wavefunction $\phi_0+\chi_s+\chi_{ss}$ *prior* to making any of the approximations which lead to the "exact pair" energies. If we do so, we of course are guaranteed that the wavefunction has exactly the correct spin properties. Following this substitution, an analysis of the energy, similar to Sinanoğlu's, can be performed, which leads to the same separation into an "exact pair" part plus small corrections.

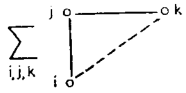
APPENDIX

In Sinanoğlu's original breakdown of the energy,[1a] a diagram technique was used to obtain the various matrix elements. The term $\langle \hat{u}_{ij}(i,j) \mid m_{ij} \mid \hat{u}_{ij}(i,j) \rangle$ can be represented diagrammatically, if one draws a solid line connecting the points i, j of $\hat{u}_{ij}$ and a dotted line for the m_{ij}, as



(A1)

The remainder[12] R then contains the three electron linked diagrams

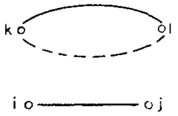


(A2)

which for the above particular labeling means

$$\langle i(i)\hat{u}_{jk}(j,k) \mid m_{ik} \mid k(k)\hat{u}_{ij}(i,j) \rangle,$$

plus additional terms, overlooked by Sinanoğlu, which arise from the diagram



(A3)

The example (A3) is the integral

$$\langle \hat{u}_{ij}(i,j) \mid \hat{u}_{kl}(i,j) \rangle \langle k(k)l(l) \mid m_{kl} \mid i(k)j(l) \rangle.$$

An estimate of this integral, for the largest term of this type in the Be atom, leads to a value of 0.0008 eV, an entirely negligible effect.[13] Thus the theory does not appear to be affected to a significant degree by such terms.

[12] See Ref. (1a), p. 716 for the definition of R.

[13] O. Sinanoğlu (in a private communication) has obtained this value for the integral, based on Watson's Be analysis (Ref. 12).